Fabrication of three-dimensional titania building blocks on glass substrate from Mono-dispersed titanium glycolate spheres and their photocatalystic properties

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Fabrication of Three-Dimensional Titania Building Blocks on Glass Substrate from Mono-Dispersed Titanium Glycolate Spheres and Their Photocatalystic Properties

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Mono-dispersed titanium glycolate sphere powders were successfully synthesized through a homogeneous nucleation and growth process. The obtained titanium glycolate sphere powders showed a fine size distribution and shape. On calcination, the titanium glycolate spheres lost chemically bound organic compounds, and changed to anatase (500°C) and rutile (900°C) titania spheres. Titania films fabricated with the synthesized titanium glycolate spheres exhibited marked photocatalytic activity and effective reusability. The fabricated films were characterized by X-ray diffraction, scanning electron microscopy, and thermogravimetric and differential thermal analyses.
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1. Introduction

One of the most urgent environmental issues is the treatment of wastewater. A combination of population growth and the rapid development of industrialization has resulted in a steady increase in water pollution.[1,2] Unfortunately, conventional wastewater treatment technologies cannot remove all contaminants.[3]

The titania photocatalyst has shown marked potential for the treatment of wastewater. The titania photocatalyst can overcome the limitations of conventional technologies by the mineralization of contaminants. The rationales of titania photocatalytic processes are based on the *in situ* generation of highly reactive transitory species, such as hydrogen peroxide, hydroxyl radicals, superoxide radicals, and ozone, for the mineralization of refractory organic compounds, water pathogens, and disinfection by-products.[4,5] Furthermore, titania has marked advantages such as its marked photo-oxidizing potential, high chemical and thermal stability, nontoxicity, low cost, and strong mechanical properties.[6] However, despite its many advantages and excellent photocatalytic properties, standard powdered titania still has limitations for use in commercial photocatalytic processing. For example: (1) its photocatalytic efficiency easily decreases due to the aggregation of titania powders, especially when they are present at high concentrations, (2) separation of the titania powders from suspension after the reaction is difficult, and (3) particulate suspensions are not easily applicable to continuous flow systems.[7] In order to overcome these limitations, titania was prepared on substrates with various morphologies of film, such as nano-rods, nano-wires, and inverse opal, for the continuous flow system.

Among the many kinds of morphology for film-type photocatalysts, the three-dimensional sphere building block is expected to increase the photocatalytic properties. The three-dimensional sphere building block has a large surface area and sufficient space between the spherical titania powders. The large surface area increases opportunities to degrade waste water, and the space between spherical powders makes the process of the chemical reaction much easier because of reactant and product molecules moving in or out of the titania powders. The method to synthesize mono-dispersed sphere titania is an important part of the fabrication of three-dimensional titania building blocks via a self-assembly.[8–10] Until recently, the synthesis of mono-dispersed spheres has been limited to polymers and silica. Only a few experiments have attempted the synthesis of mono-dispersed titania by chemical methods, such as sol–gel,[11–14] hydrothermal,[15,16] aerosol,[17] and micro-emulsion.[18,19] Furthermore, the deposition of titania nano-particles on mono-dispersed polystyrene or silica spheres has also been studied.[20,21] Despite some success, limitations still exist, including particle aggregation, a wide size distribution, and multiple-step procedures or critical reaction conditions.

In this study, we report the synthesis of mono-dispersed titania sphere powders using a mild and environmentally friendly process. Also, the fabrication of three-dimensional titania building blocks on a glass substrate using the synthesized mono-dispersed titania spheres and their photocatalytic properties are described.

2. Experimental Procedure

2.1 Substrate preparation

A piece of glass (5 × 15 mm) was ultrasonically cleaned in Di-water, ethanol, and acetone for 10 min, respectively. The well-cleaned glass substrate was immersed in piranha solution (2 : 1 mixture of concentrated H_2SO_4/30% H_2O_2) and heated at 80°C for 2 h. Then, it was immersed in hydroxide solution to remove organic matter, and to create a hydrophilic surface.

2.2 Synthesis of titanium glycolate sphere powders

In a vial, 25 mM tetra-n-butyl titanate (TBT, Sigma-Aldrich) was added to 20 mL of ethylene glycol (99.8%, Sigma-Aldrich). The solution was magnetically stirred for 12 h at room temperature, and then poured into 10 mL of acetone (99.99%, Sigma-Aldrich) containing 20 µL of

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poly(oxyethylene) nonylphenyl ether (IGEPAL® CO-630, Sigma-Aldrich) as a surfactant. The solution was stirred at 1,000 RPM for 5 min, and it was aged for 5 days. After aging, the white precipitate was harvested by centrifugation, followed by washing with distilled water 3 times to remove the ethylene glycol and surfactant.

2.3 Characterization of titanium glycolate sphere powders

The X-ray diffraction measurement, which was used to characterize the crystalline phase of the titanium glycolate sphere powders, was carried out using an X-ray diffractometer (XRD, PANalytical, X'pert PRO) with CuK_α radiation over the 2θ range from 5° to 80° at a scan rate of 2°/min. The morphology of the prepared film was observed using scanning electron microscopy (SEM, JEOL, JSM-6510LV). The thermal properties of the titanium glycolate spheres were measured by thermogravimetric and differential thermal analyses (TG-DTA, Rigaku Corporation, Thermo plus TG 8120) in air at a heating rate of 5°C/min over a temperature range of 30–1200°C.

2.4 Synthesis of titania nano-powders

For synthesis, 0.2 M titanium isopropoxide was slowly dropped into 50 mL of Di-water. After 1 h of stirring, the white precipitate was separated and washed with Di-water 3 times. The white precipitate was peptized in Di-water containing 0.2 M of tetramethylammonium hydroxide (99.8%, Sigma-Aldrich) by ultra-sonication for 24 h. After the peptization, the solution was placed in a Teflon-lined stainless-steel autoclave (TVS-N2, 125 mL, TAIATSU TECHNO® Corp., Tokyo, Japan). After sealing, the solution was heated at 200°C for 1 h, and allowed to cool to room temperature. The obtained titania nano-powders were washed three times with di-water.

2.5 Preparation of opal and inverse opal structure of titania film on the glass substrate

The prepared glass substrate was vertically suspended in a vial containing 1 mL of 1.5 vol% titanium glycolate sphere powder suspension and 1 mL of 1.5 vol% titania nano-powder suspension (Fig. 1(A)). The titanium glycolate sphere powder/titania nano-powder suspension was allowed to evaporate slowly over a period of 1 day at 60°C, to allow the deposition of the thin film onto the suspended substrate.

2.6 Preparation of the Degussa P-25 titania layer on the glass substrate

Degussa P-25 powder was adopted as a reference for comparison. Degussa P-25 titania is the most commonly used commercial photocatalytic material, exhibiting marked photocatalytic activity.[20,21] Firstly, 2 g of P-25 powder was ground with 10 mL of ethanol, 5 mL of H_2O, and 10 mass% of polyethylene glycol (PEG, Mw 2,000, Sigma-Aldrich) in an agate mortar for 30 min. The P-25 titania film was prepared by depositing the paste on a fresh piece of glass substrate using a roll-coating method. The film thickness was controlled using adhesive tape (3M, CC 1820-D-J, thickness: 50 μm) that had previously been applied to the edges of the glass substrate. After the P-25 titania film had been deposited, it was dried at room temperature and calcined at 450°C for 30 min in air.

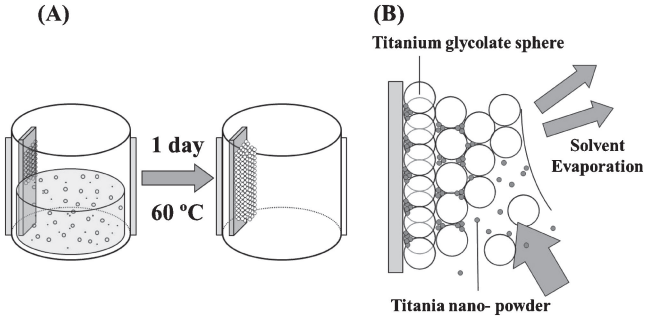

Fig. 1 (A) Schematic of evaporative deposition of a three-dimensional sphere building block film. (B) Illustration of the co-assembly method of titanium glycolate sphere powder self-assembly in the presence of a titania nano-powder solution.

2.7 Analysis of photocatalytic activity

The photocatalytic activity of the titania film on the glass substrate was investigated by measuring the photodegradation rate of rhodamine B (RhB, 90%, Sigma-Aldrich) in aqueous solution. The photocatalytic reaction was carried out in a 10-mL polymer vessel under a UV lamp, with the distance between the vessel and UV lamp being 10 cm, after 5 mL of RhB aqueous solution (20 μM) and the six pieces of prepared film had been placed in the reaction vessel. At the specified intervals of UV illumination, a specimen of RhB aqueous solution was collected and analyzed using a UV-vis spectrophotometer (Shimadzu, UV-2450).

3. Results and Discussions

To investigate the effect of the surfactant on the size and morphology of titanium glycolate sphere powders, the precursors were synthesized with various concentrations of surfactant. Figure 2 shows SEM images of the titanium glycolate sphere powders synthesized using different concentrations of surfactant over 3 days of aging. It was difficult to obtain mono-dispersed titanium glycolate sphere powders without surfactant (Fig. 2(A)). When surfactant was added, the size distribution and shape of titanium glycolate spheres largely improved, as shown in Fig. 2(D). It is to be expected that surfactant is adsorbed strongly to the surface of titanium glycolate spheres. The polyoxyethylene group of the surfactant functions as the anchoring moiety. The polyoxyethylene groups remain free in the external aqueous environment and can give rise to colloidal stability by a repulsion effect through a steric enthalpic-entropic mechanism of stabilization.

Figure 3 shows SEM images of the titanium glycolate sphere powders synthesized with various aging times. The spherical particles can be observed to form within a short time after adding the titanium glycolate solution to the acetone (Fig. 3(A)). After 1 day of aging, the particle size increased to 340 from 110 nm. After 2 days of aging, the size distribution and shape of titanium glycolate spheres were improved, but there was no further increase in the particle size. We can obtain mono-dispersed titanium glycolate sphere powders after 3 days of aging.

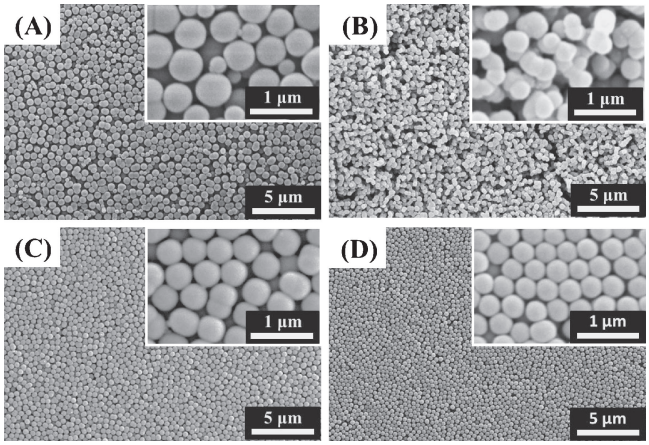

Fig. 2 SEM photomicrographs of titanium glycolate sphere powders synthesized using different concentrations of surfactant: (A) 0 μL, (B) 5 μL, (C) 10 μL, and (D) 20 μL.

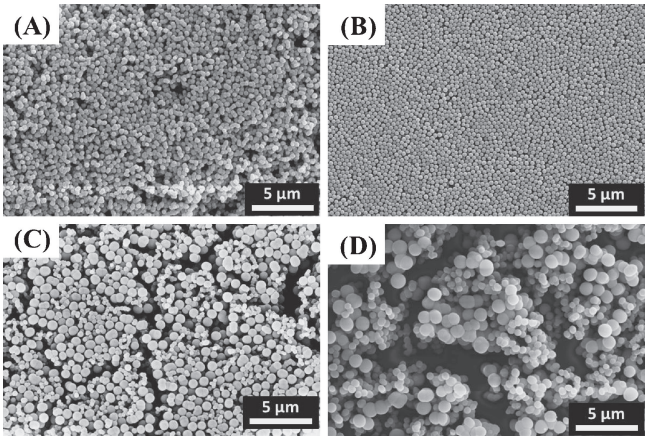

Fig. 4 SEM photomicrographs of titanium glycolate sphere powders synthesized at different reaction temperatures: (A) 0°C, (B) 20°C, (C) 40°C, and (D) 60°C.

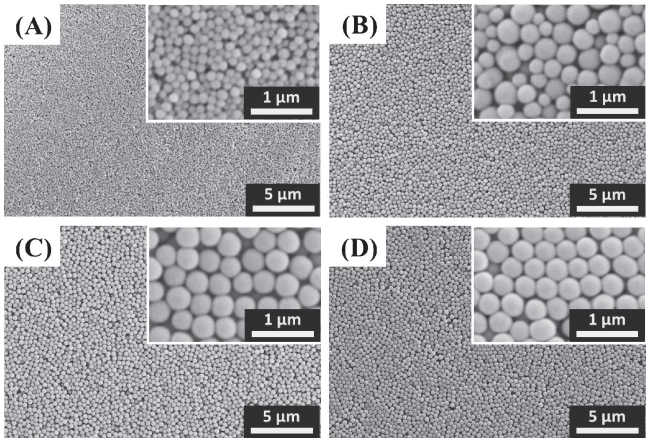

Fig. 3 SEM photomicrographs of titanium glycolate sphere powders synthesized with different aging times: (A) 30 min, (B) 1 day, (C) 2 days, and (D) 3 days.

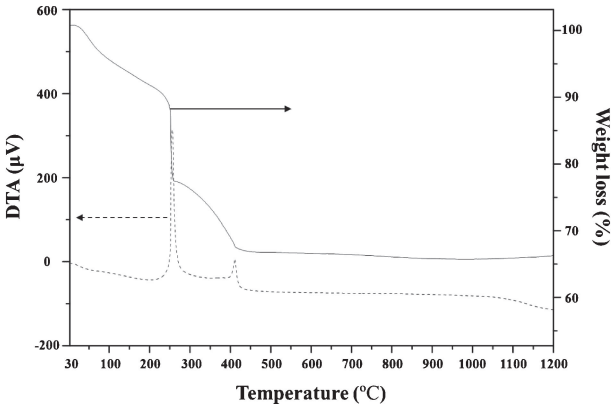

Fig. 5 TG-DTA curves of titanium glycolate sphere powders synthesized at 20°C for 3 days using 20 μL of surfactant.

Figure 4 shows SEM images of titanium glycolate spheres synthesized using 20 μL of surfactant for 3 days with different reaction temperatures. Figure 4(A) and (B) show a difference in the particle morphology when the reaction occurred at 0°C and 20°C. The shapes of titanium glycolate spheres that reacted at 0°C were irregular compared to titanium glycolate spheres that reacted at 20°C. With the temperature increase, the particle size of titanium glycolate sphere increased significantly, as shown in Fig. 4(C) and (D). We believe that the frequency of collision between the small titanium glycolate spherical particles increased as the temperature was raised, and thus led to the formation of larger titanium glycolate spherical particles. For the synthesis of mono-dispersed titanium glycolate sphere powders, 20°C may be optimal.

The titanium glycolate sphere powders were investigated by TG-DTA and XRD measurements to confirm their thermal properties. Figure 5 shows TG-DTA analysis results for titanium glycolate spheres synthesized at 20°C for 3 days using 20 μL of surfactant. The total weight loss of the titanium glycolate sphere powders was 34.2 mass%, due to three factors. The first region under 200°C corresponds to the removal of physically adsorbed water and the desorption of coordinately bound water or physically bound residual ethylene glycol. The sharp weight loss of the second region at 250°C with an exothermic peak is attributed to the decomposition of organic ligands, such as ethylene glycol units and remaining organic residues. The third slow weight loss between 250°C and 410°C is associated with the degradation of organic ligands that are probably located in the inner part of the titanium glycolate spheres, thus requiring higher temperatures and longer processing.[22] At 410°C, one exothermic peak was not accompanied by any weight loss, indicating phase transformation to anatase titania.

XRD analysis was performed to examine the phase transformation of titanium glycolate spheres before and after calcination at various temperatures for 2 h. Figure 6 shows XRD patterns of the as-synthesized titanium glycolate spheres and titania spheres calcined at various temperatures. The diffraction peaks of the as-synthesized titanium glycolate spheres indicated an amorphous phase, and it remained until being calcined at 300°C. The single phase of anatase (JCPDS 21-1272) became discernible at 500°C, and a continuously rutile phase appeared at 700°C, coexisting with the anatase phase. It became a single rutile phase (JCPDS 21-1276) at 900°C. The phase transformation from anatase to rutile occurred gradually with no clear thermal effect seen in DTA curves.

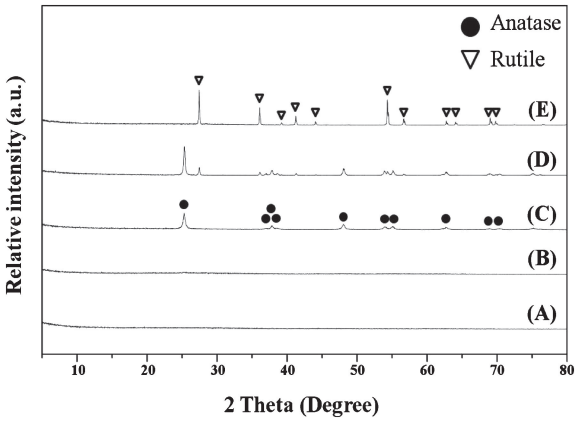

Fig. 6 XRD patterns of titanium glycolate sphere powders clacined at different temperatures for 2 h: (A) As Syn. (titanium glycolate), (B) 300°C (amorphous), (C) 500°C (anatase), (D) 700°C (anatase and rutile), and (E) 900°C (rutile).

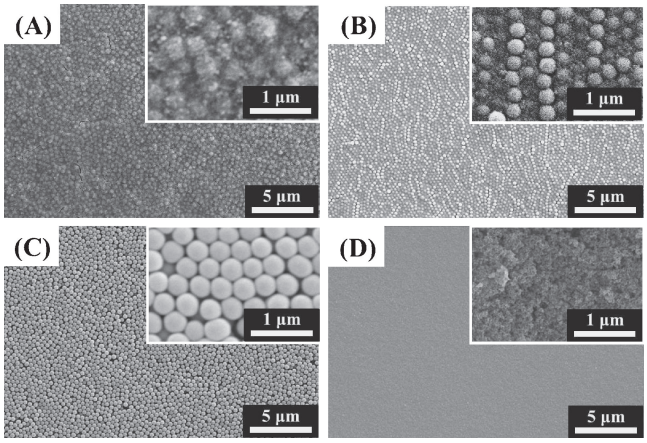

Fig. 7 SEM photomicrographs of various morphologies of titania film fabricated using: (A) titanium glycolate spheres/titania nano-powder, (B) polystyrene spheres/titania nano-powder, (C) titanium glycolate spheres, and (D) P-25.

Figure 7 shows titania films fabricated with various morphologies for the comparison of photocatalytic properties. The titania films fabricated with titanium glycolate spheres/titania nano-powder (Fig. 7(A)) and polystyrene spheres/titania nano-powder (Fig. 7(B)) have a similar morphology. Both films show that titania nano-particles are covered with the spherical particles. After heat treatment, the titanium glycolate spheres were transformed into the anatase titania spheres, and they exist as part of the film (Fig. 8(A)). However, the polystyrene spheres were burned out, so the polystyrene spheres/titania nano-powder film becomes an inverse opal film (Fig. 8(B)). Figure 7(C) shows that the film is composed of mono-dispersed titanium glycolate spheres. After heat treatment at 600°C for 2 h, the titanium glycolate spheres were change to anatase titania spheres (Fig. 8(C)). Compared with titanium glycolate spheres, the surface of titania spheres was slightly roughened because of the removal of ethylene glycol during heat treatment. Also, the size of titania spheres was deceased to 260 from 340 nm.

The degradation of RhB in aqueous solution was studied to investigate the photocatalytic properties of titania film. Changes in the characteristic absorption peak of RhB

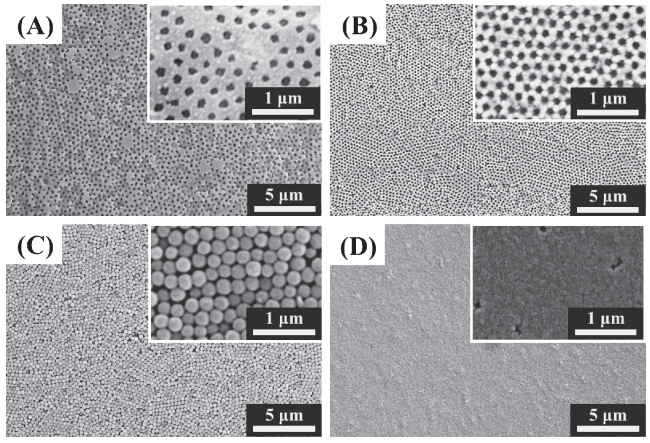

Fig. 8 SEM photomicrographs of various morphologies of titania films after heat treatment fabricated using: (A) titanium glycolate spheres/titania nano-powder, (B) polystyrene spheres/titania nano-powder, (C) titanium glycolate spheres, and (D) P-25.

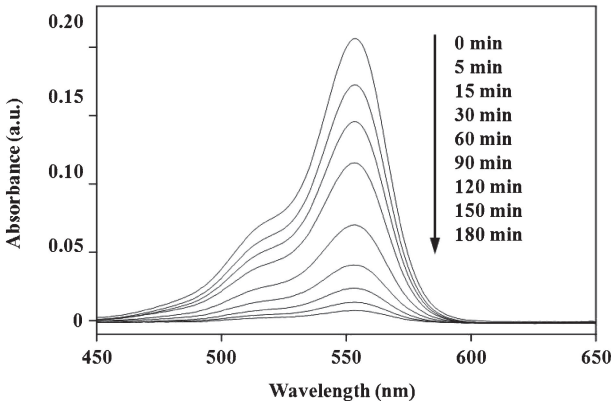

Fig. 9 Absorbance spectra of RhB solution after treatment with titania film fabricated with titanium glycolate spheres/titania nano-powder.

($\lambda = 554$ nm) were observed by UV-vis spectrometry to confirm its degradation. The absorption spectra of RhB aqueous solution, which was photo-degraded at different irradiation times by titania film fabricated using the titanium glycolate spheres/titania nano-powders, are shown in Fig. 9. The intensity of the absorption spectra of RhB decreased continuously with the increase in the irradiation time.

Figure 10 shows degradation curves of RhB dye solution after treatment with titania films, which have different shapes. RhB degraded only 6% without the photocatalyst over the 180-min time interval, indicating that RhB degrades very slowly when alone and under UV-light irradiation. The photocatalytic properties of titania films, which have different morphologies, were not significantly different. All kinds of titania film show excellent photocatalytic activities to decompose RhB. The decomposition of RhB on titania films was so fast that the diffusion of RhB determined the decomposition rate.

The reusability test was carried out over five successive cycles of the RhB degradation experiment with the titania film fabricated using the titanium glycolate spheres/titania nano-powders, and the results are shown in Fig. 11. The RhB was degraded in every cycle with an almost constant photodecomposition rate. These results show that the titania

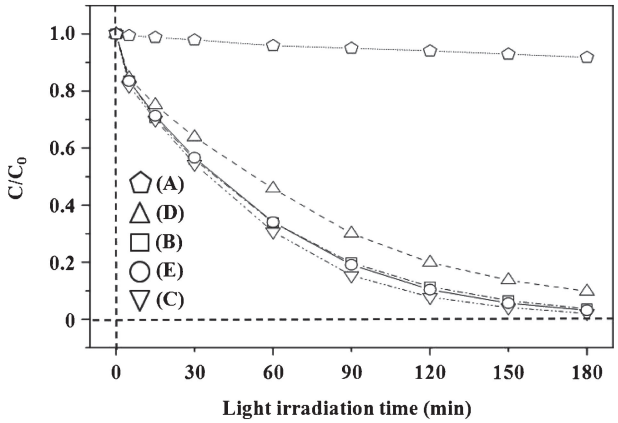

Fig. 10 Degradation curves of RhB dye solution after treatment with titania films fabricated with various morphologies: (A) without photocatalyst, (B) titanium glycolate spheres/titania nano-powder, (C) polystyrene spheres/titania nano-powder, (D) titanium glycolate spheres, and (E) P-25.

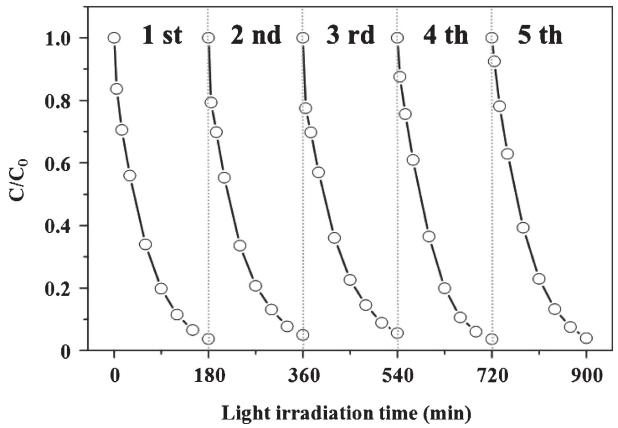

Fig. 11 Cyclic degradation curves of RhB dye solution after treatment with titania film fabricated with titanium glycolate spheres/titania nano-powder.

film is highly stable in a photochemical environment and effectively reusable with the photocatalyst.

4. Conclusion

The mono-dispersed titanium glycolate sphere powders were successfully synthesized using titanium glycolate solution as a reactant and acetone as a solvent. Adding a surfactant, poly(oxyethylene) nonylphenyl ether, is highly effective for controlling the size distribution of titanium glycolate sphere powders. The titania films fabricated with various morphologies can be successfully converted to anatase-phase titania by calcination at 500°C. The titania films showed excellent photocatalytic properties and stable durability for the decomposition of RhB under UV-light. It is anticipated that the titania films will be applied for continuous flow wastewater treatment systems.

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